APPLICATION OF CYCLIC VOLTAMMETRY

TO A CE MECHANISM IN A NATURAL WATER

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Introduction

In speciation studies in natural waters the kinetic aspect has to be considered since we are dealing with dynamic systems. In this context the kinetics of dissociation of heavy metal complexes with some naturally occurring aminoacids has been analysed.

In a general way the aminoacids do not dominate the complexation of trace metals such as copper(II), lead(II), Cadmium(II) and zinc(II), but these complexes can exist adsorbed on particles and in some estuarine, coastal and interstitial waters, where the concentration of dissolved organic matter (DOM) may reach values up to a few hundreds of mg C/l.

It is well known that cyclic voltammetry (CV) is quite a suitable method to do kinetic studies since the scan rate v (time scale of the technique) can be easily changed of several orders of magnitude. So CV was used with the hanging mercury drop electrode to determine the rate constants of dissociation in the non-complexing medium of $NaClO_4$ at the ionic strength of seawater (0.70 M) and in synthetic seawater in order to ascertain the influence of the major salinity components, namely the chloride ion and the alkaline earth metals Ca(II) and Mg(II).

The CE mechanism

The kinetic studies were carried out for the systems in Table 1 where the adsorption mechanism was not superimposed.

Table 1

Cd(II) + Glutamic Ac.	Zn(II) + Glutamic Ac.
Cd(II) + Aspartic Ac.	Zn(II) + Aspartic Ac.
	Zn(II) + Glycine

The CE mechanism is easily recognized by the voltammograms shown in Fig. 1 for the system Zn(II) + Glutamic Acid (in $NaClO_4$) for different values of v . In this figure wave I is due to the reduction of the metal ion coming from the dissociation of the complex, wave II involves the direct reduction of the complex (es) and in the reverse scan wave II corresponds to $Zn(Hg) \rightleftarrows Zn(II) + 2e$. As v is increasing the current of wave I decreases while that of wave II increases, since there is less time for the dissociation of the complexes.

Determination of the rate constants of dissociation k_d

The determination of k_d values involves a plot of i_d/i_k versus v according to

Fig. 1

(Current/μA vs POTENCIAL VS SSCE/mV; curves labelled 20, 200, 2000, 20000; axis marks −900, −1100)
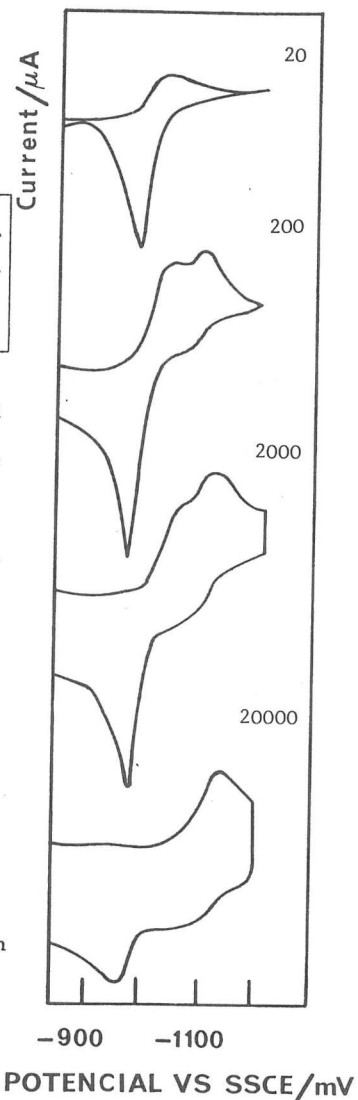
$$i_d/i_k = 1.02 + 0.471 \left(\frac{nF}{RT}\right)^{1/2} \sigma \, (v/\ell)^{1/2} \qquad (1)$$

valid for a reversible charge transfer and where i_d and i_k are the diffusion and kinetic currents respectively, ℓ is the sum of the pseudo rate constants and σ is given by the ratio of the non-electroactive and the electroactive species.

The i_d values can be determined either from the reduction wave in the absence of ligand assuming the similarity of the diffusion coefficients of the metal and the complexes, or from the second reduction wave at large values of v. Because wave II involves an irreversible electron transfer the following equation has to be considered

$$i_p^{\,rev} = i_p^{\,irrev} \frac{0.446}{0.496} \frac{1}{\sqrt{\alpha}} \qquad (2)$$

the charge transfer coefficient α being determined from the variation of the peak potential with v.
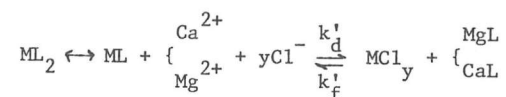
While cadmium reduction is reversible for the scan rates considered, the same is not true for zinc that behaves as a quasi-reversible system, i.e., even in the absence of ligand i_p/v decreases with v. Although equation (1) is only valid for reversible systems, the ratio i_d/i_k can still be used since i_d (the diffusion current is the absence of ligand) and i_k are both affected in the same way by the quasi-reversible reduction of Zn(II).
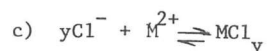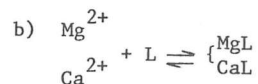
In $NaClO_4$ the following scheme

$$ML_2 \leftrightarrow ML \; \underset{k_f}{\overset{k_d}{\rightleftharpoons}} \; M^{2+} + L$$
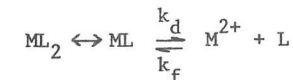
has been postulated. On the other hand in synthetic seawater the

global reaction

$$ML_2 \leftrightarrow ML + \left\{ \begin{array}{c} Ca^{2+} \\ Mg^{2+} \end{array} \right. + yCl^- \underset{k_f'}{\overset{k_d'}{\rightleftharpoons}} MCl_y + \left\{ \begin{array}{c} MgL \\ CaL \end{array} \right.$$

can be considered the sum of the following steps.

a) $ML \rightleftharpoons M^{2+} + L$

b) $\begin{array}{c} Mg^{2+} \\ Ca^{2+} \end{array} + L \rightleftharpoons \left\{ \begin{array}{c} MgL \\ CaL \end{array} \right.$

c) $yCl^- + M^{2+} \rightleftharpoons MCl_y$

According to these mechanisms and considering the fact that $\beta_{MgL} |Mg| > \beta_{CaL} |Ca|$ the following expressions have been deduced (Table 2) and their validity confirmed by the constant values of k_d obtained (Table 3).

Table 2

NaClO$_4$ 0.70 M	Synthetic Seawater
$\rho_d = k_d \dfrac{|ML|}{|ML| + |ML_2|}$	$\rho_d' = k_d' \dfrac{|ML|}{|ML| + |ML_2|} |Mg| \, |Cl|^y$
$\rho_f = k_d \, \beta_1 \, |L|$	$\rho_f' = k_f' \, |L| \, \beta_{MgL} |Mg| \, \beta_{MCl_y} |Cl|^y$
a) $\sigma = \dfrac{|ML_2| + |ML|}{|M|}$	$\sigma = \dfrac{|ML_2| + |ML|}{|M|}$
$|L| = \dfrac{C_L}{1 + \beta_1^H |H|}$	$|L| = \dfrac{C_L}{1 + \beta^H |H| + \beta_{MgL} |Mg^{2+}|}$

a) The expression of σ is the same in both cases since the chloro-complexes are completely labile species.

Results and discussion

The values presented in Table 3 are compatible with the Eigen's mechanism for complex formation, i.e., the rate determining step is the loss of water molecules of hydration sphere of the metal and so k_f is of the order of $10^8 - 10^9$ $M^{-1}s^{-1}$ and   does not depend significantly on the ligand. From the constancy of the values obtained for different pH we can conclude that the proton is not involved in the dissociation step. On the other hand the presence of Cl^- and alkaline earth ions accelerates the dissociation of the ML species due to the formation of chlorocomplexes and magnesium complexes.

Table 3

MEDIUM / COMPLEX	NaClO$_4$ 0.70 M	Synthetic Seawater
	k_d/s^{-1}	k_d'/s^{-1}
Cd + Glutamic Acid	$(4 \pm 1) \times 10^5$	$(1 \pm 0.5) \times 10^7$
Cd + Aspartic Acid	$(2 \pm 1) \times 10^4$	$(3.2 \pm 0.8) \times 10^6$
Zn + Glycine	$(1.9 \pm 0.5) \times 10^3$	$(5 \pm 2) \times 10^4$
Zn + Glutamic Acid	$(2.0 \pm 0.5) \times 10^3$	$(7 \pm 2) \times 10^4$
Zn + Aspartic Acid	$(4 \pm 1) \times 10^2$	—

References

M.L. Simões Gonçalves, M.M. Correia dos Santos
The Science of the Total Env., 76 (1988) 1.